17

ON THE ABSORPTION OF 3.18-CM MICROWAVES IN SOME ALIPHATIC ALCOHOLS AND THEIR SOLUTIONS*

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ABSTRACT. The dependence on temperature of absorption of microwaves of wavelength 3.18 cm in *n*-propyl, *n*-butyl, isopropyl-, isobutyl-, *n*-octyl- and *n*-heptyl alcohol and in their solutions in CCl_4 and heptane at different concentrations have been studied by simple optical method.

It is observed that in the case of lower alcohols absorption increases with the increase of temperature without showing any definite maximum in the curve, while the higher alcohols and the solutions of all the six alcohols show absorption maxima at temperatures depending on their viscosities.

From a comparison of different results it has been concluded that most of the molecules in the lower alcohols in the pure state are in the form of dimers which break up in the solutions into single molecules. In the case of higher alcohols the molecules being large, some of the molecules do not form such dimers and remain as single molecules.

Applying Debye's theory the radius of the rotor has been calculated, and the value has been found to be near about 1.96 A in all the cases. The rotor has been indentified with the OH group.

INTRODUCTION

The anomalous dielectric dispersion in alcohols in the region of radio-waves of wave-lengths ranging from decimetre to metre region was studied by Mizushima (1927). He found that some aliphatic alcohols show absorption in the metre region and the region of such anomalous dispersion shifts towards longer wavelengths as the length of the molecule increases. With a particular frequency he observed (Mizushima, 1929) that the temperature at which the maximum absorption occurs becomes higher for higher alcohols. He concluded that the theory proposed by Debye (1913) correlating time of relaxation with the dielectric constant at any frequency was verified by these results and that the whole molecule was the rotor in these cases. Later, Ghosh (1954, 1955) studied the absorption of 3.18cm microwaves in some aromatic liquids with the molecules having OH group as a

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substituent and by varying the temperature of the liquids he observed maximum absorption at a particular temperatue in each case. From the values of the time of relaxation and the viscosity of the liquids at those temperatures he calculated the radius of the rotor and found it to be of the order of 1.5 A. He concluded that the rotor was the OH group and not the whole molecule in these cases.

Recently, Imanov and Abbasov (1957) used microwaves of wave-lengths ranging from 10 cm to 180 cm to measure the dielectric loss in several normal and iso-alcohols in this region. They observed maximum loss at particular wave-lengths in the region from 18 cm to 60 cms in five alcohols, but no such maxima were observed in methyl and ehtyl alcohol in the whole wave-length range 12 cm—180 cm. They did not identify the rotor in the above cases.

It would be interesting, however, to find out whether in these pure aliphatic alcohols in the liquid state the OH group has any freedom of rotation and whether the influence of solvents affects such freedom. With this object in view the absorption of 3.18 cm microwaves in a few aliphatic alcohols in the liquid state and also in solution in suitable solvents has been investigated.

EXPERIMENTAL

The experimental arrangements and procedure adopted in the present investigations were the same as those used previously (Bhattacharyya 1958). The liquids used were *n*-propyl-, *n*-butyl-, isopropyl-, isobutyl-, *n*-heptyl-, and *n*-octyl alcohol. In order to make the alcohols free from water the lower alcohols were mixed with dehydrated magnesium sulphate and were kept in this condition for two days. After filtration they were treated with fresh quick-lime and subjected to fractional distillation. The two higher alcohols were distilled in vacuum after proper dehydration. The absorption was studied in the pure liquids as well as in their solutions of different concentrations in CCl_4 and heptane in the range of temperature from 28°C to 140°C. The graphs showing the relation between temperature and the attenuation coefficients of different liquids were drawn. The values of static dielectric constant, refractive indices and coefficients of viscosity for the pure liquids were obtained from the standard tables. These data for the solutions were determined experimentally. With the help of Debye's theory and using these data, the radius of rotor was calculated in each case.

RESULTS AND DISCUSSIONS

Fig. 1 shows the temperature-dependence of the attenuation coefficients of pure alcohols. The lower alcohols like *n*-butyl-, *n*-propyl-, isobutyl- and isopropyl alcohol do not show any absorption maxima. The absorption in these cases increases rapidly with the increase of the temperature. Similar results were also obtained in the case of pure ethylene chlorhydrin (Bhattacharyya, 1959). The higher alcohols, however, show definite absorption maxima. Octyl alcohol

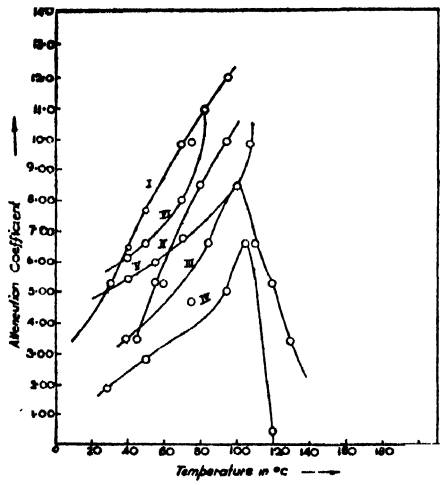

Fig. 1. Temperature dependence of the attenuation coefficient for pure alcohols

I—*n*-Propyl alcohol.
II—*n*-Butyl alcohol.
III—*n*-Heptyl alcohol.
IV—*n*-Octyl alcohol.
V—iso-Butyl alcohol.
VI—iso-Propyl alcohol.

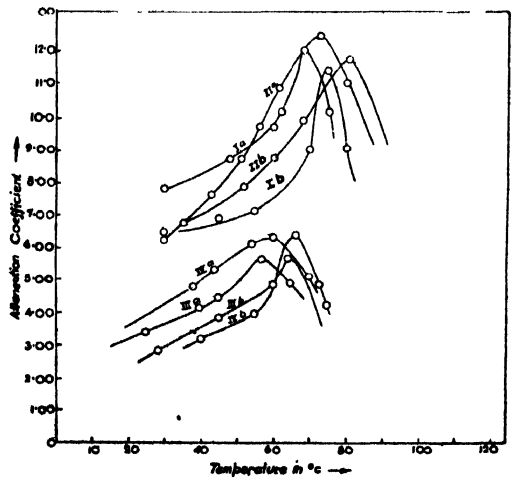

Fig. 2. Temperature dependence of the attenuation coefficient of the solutions of *n*-alcohols in CCl_4.

Ia—20% solution of heptyl alcohol in CCl_4.
Ib—30% „ „ „ „ „ „
IIa—20% solution of octyl alcohol in CCl_4.
IIb—30% „ „ „ „ „ „
IIIa—30% solution of propyl alcohol in CCl_4.
IIIb—50% solution of butyl alcohol in CCl_4.

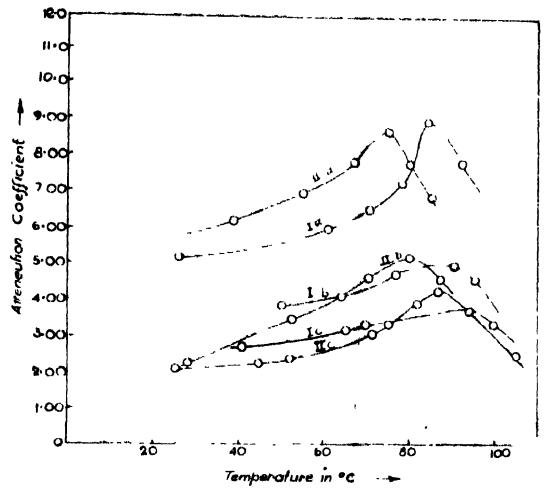

Fig. 3. Temperature dependence of the attenuation coefficient of the solution of iso-alcohols in CCl_4.

Ia—30% solution of isopropyl alcohol in CCl_4.
Ib—50% ,, ,, ,, ,, ,, ,,
IIa—30% solutions of isobutyl alcohol in CCl_4.
IIb—50% ,, ,, ,, ,, ,, ,,

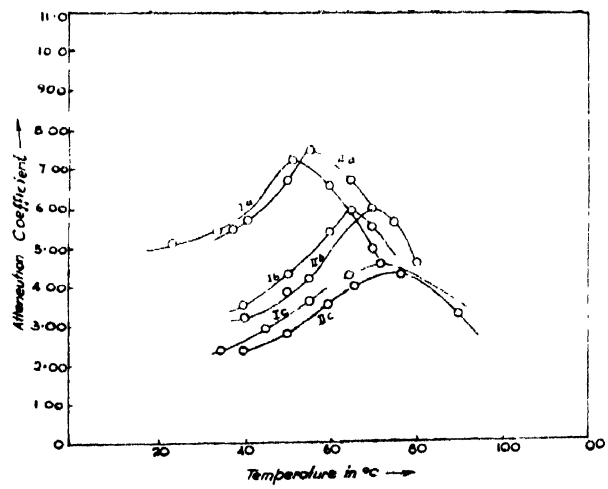

Fig. 4a. Temperature dependence of the attenuation coefficient of the solutions of lower alcohols in heptane.

Ia—30% solutions of *n*-proypl alcohol in heptane.
Ib—50% ,, ,, ,, ,, ,,
Ic—70% ,, ,, ,, ,, ,,
IIa—30% solutions of *n*-butyl alcohol in heptane.
IIb—50% ,, ,, ,, ,, ,,
IIc—70% ,, ,, ,, ,, ,,

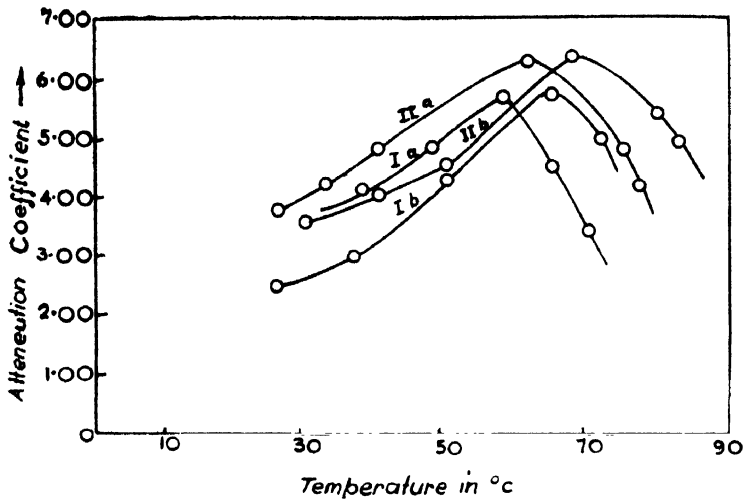

Fig. 4b. Temperature dependence of the attenuation coefficient of the solutions of higher alcohols in heptane.

Ia—30% solutions of octyl alcohol in heptane.
Ib—50% ,, ,, ,, ,, ,, ,,
Ic—70% ,, ,, ,, ,, ,, ,,
IIa—30% solutions of heptyl alcohol in heptane.
IIb—50% ,, ,, ,, ,, ,, ,,
IIc -70% ,, ,, ,, ,, ,, ,,

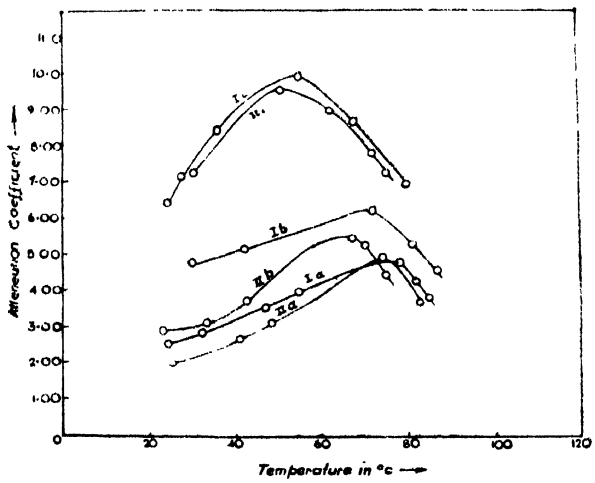

Fig. 5. Temperature dependence of the attenuation coefficient of the solutions of iso-alcohol in heptane.

Ia—70% solution of isobutyl alcohols in heptane.
Ib—50% ,, ,, ,, ,, ,, ,,
Ic—30% ,, ,,
IIa—70% solution of isopropyl alcohol in heptane.
IIb—50% ,, ,, ,, ,, ,, ,,
IIc—30% solution of isopropyl alcohol in heptane.

shows the maximum at 105°C while heptyl alcohol shows it at 100°C. The absence of any absorption maxima in the case of lower alcohols cannot be explained on the assumption that these occur at higher temperatures i.e. at temperatures higher than 100°C, because heptyl and octyl alcohols which have higher viscosity show their respective maxima near about 100°C. When the lower alcohols are dissolved in the solvents, carbon tetrachloride and heptane we get absorption maxima at certain temperatures as shown in Figs. 2, 3, 4 and 5. This difference in the behaviour of the pure liquids and solutions may be explained on the assumption that in the pure liquid most of the molecules are in the form of dimers formed by weak linkage through the H-O—H-O bond and as the dimers break up with the rise of temperature contribution to absorption from new single molecules increases gradually without attaining a constant value. In the case of the higher alcohols, however, the molecules being long, some of the molecules do not form dimers and exist as single molecules. As the viscosity attains the proper value with the rise of temperature of the liquid a maximum absorption is exhibited by these molecules in these cases.

An attempt was made to calculate the radius of the rotor from Debye's theory in the cases in which maximum absorption has been observed. The data required for this purpose as well as the values of τ, the time of relaxation and a, the radius of the rotor are given in Table I. It is interesting to note that the values of a, the radius of the rotor, is almost the same in all these cases, the mean value being about 1.96 Å. Evidently, the rotor is not the whole molecule in any of the liquids and the solutions and the common group present in the molecules being the OH group, the rotor may be identified with this group. In previous investigations the radius of the rotor for the OH group in aromatic compounds was calculated and it was found to be of the order of 1.5A (Ghosh, 1955a, 1954), but no such data for aliphatic alcohols are available. It cannot be expected that radius of the OH group as the rotor in the case of aliphatic compounds should be the same as that for the aromatic compounds, as the radius of such rotor is expected to be dependent on the bond angle and other factors. Ghosh (1955a) observed in *o*-methoxy phenol, a typical aromatic compound, the radius of the OH rotor to be 1.7A which is slightly larger than the value observed in the case of *p*-chlorophenol, *p*-chlorocresol etc., So, the rotor in the present case can be identified with OH group of the alcohol molecules.

The comparison of the curves for the pure liquids with those for their solutions thus leads to the conclusion that in the lower alcohols in the pure state most of the molecules are in the state of loosely coupled dimers and in the solutions these dimers break up into single molecules. Application of Debye's method in these cases gives consistent results and also furnishes much information about the state of association of the molecules in the liquids.

TABLE I

Substance	Concentration	ε	$\sqrt{\varepsilon_0}$	Temperature	100γ	$\tau \times 10^{11}$ sec	$a \times 10^8$ cm.
Propyl alcohol	30%	6.57	1.44	57°C	0.6886	1.42	1.95
+ CCl_4	50%	8.60	1.44	64°C	0.7317	1.32	1.83
Butyl alcohol	30%	4.66	1.44	60°C	0.6910	1.55	2.00
+ CCl_4	50%	6.30	1.42	66°C	0.7531	1.45	1.93
Isopropyl alcohol	30%	7.54	1.43	58°C	0.6913	1.38	1.94
+ CCl_4	50%	11.1	1.42	65°C	0.6035	1.22	1.96
Isobutyl alcohol	30%	4.93	1.44	62°C	0.7333	1.53	1.97
+ CCl_4	50%	5.75	1.43	68°C	0.7197	1.48	1.97
Heptyl alcohol	30%	3.80	1.45	75°C	0.8402	1.61	1.94
+ CCl_4	20%	3.28	1.45	68°C	0.7957	1.64	1.97
Octyl alcohol	30%	3.56	1.45	81°C	0.8572	1.62	1.92
+ CCl_4	20%	3.12	1.45	73°C	0.8024	1.65	1.98
Heptyl-alcohol	Pure	4.20	1.43	100°C	0.8000	1.58	2.01
Octyl alcohol	Pure	3.40	1.43	105°C	0.8800	1.63	1.97
Propyl alcohol	70%	10.97	1.39	72°C	0.6028	1.22	1.97
+ heptane	50%	9.50	1.39	65°C	0.6001	1.28	1.99
	30%	8.68	1.39	51°C	0.6031	1.32	1.98
Butyl alcohol	70%	9.50	1.39	76°C	0.6446	1.28	1.97
+ heptane	50%	8.85	1.39	70°C	0.6206	1.31	1.99
	30%	8.20	1.39	55°C	0.6200	1.34	1.98
Isopropyl alcohol	70%	14.54	1.39	74°C	0.6021	1.10	1.91
+ heptane	50%	10.90	1.39	68°C	0.5962	1.22	1.97
	25%	8.95	1.39	50°C	0.5785	1.31	2.00
	70%	10.57	1.39	78°C	0.6387	1.24	1.96
Isobutyl alcohol	50%	9.65	1.39	72°C	0.6204	1.28	1.98
+ heptane	25%	8.25	1.39	55°C	0.6194	1.34	1.98
Heptyl alcohol	75%	4.45	1.43	87°C	0.8999	1.56	1.90
+ heptane	50%	3.82	1.41	80°C	0.8762	1.61	1.92
	30%	3.42	1.40	75°C	0.8222	1.63	1.96
Octyl alcohol	75%	3.95	1.43	95°C	0.8704	1.60	1.95
+ heptane	50%	3.45	1.41	90°C	0.8418	1.63	1.98
	30%	3.12	1.40	84°C	0.8303	1.65	1.98

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